Geochemistry Geophysics Geosystems G3

Article
Volume 13, Number 12
13 December 2012
Q12005, doi:10.1029/2012GC004388
ISSN: 1525-2027

Published by AGU and the Geochemical Society

Temporal variations of geyser water chemistry in the Upper Geyser Basin, Yellowstone National Park, USA

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[1] Geysers are rare features that reflect a delicate balance between an abundant supply of water and heat and a unique geometry of fractures and porous rocks. Between April 2007 and September 2008, we sampled Old Faithful, Daisy, Grand, Oblong, and Aurum geysers in Yellowstone National Park's Upper Geyser Basin and characterized temporal variations in major element chemistry and water isotopes ($\delta^{18}O$, δD, ^{3}H). We compare these temporal variations with temporal trends of Geyser Eruption Intervals (GEI). SiO_2 concentrations and geothermometry indicate that the geysers are fed by waters ascending from a reservoir with temperatures of ~190 to 210°C. The studied geysers display small and complex chemical and isotopic seasonal variations, and geysers with smaller volume display larger seasonal variations than geysers with larger volumes. Aurum and Oblong Geysers contain detectable tritium concentrations, suggesting that erupted water contains some modern meteoric water. We propose that seasonal GEI variations result from varying degrees of evaporation, meteoric water recharge, water table fluctuations, and possible hydraulic interaction with the adjacent Firehole River. We demonstrate that the concentrations of major dissolved species in Old Faithful Geyser have remained nearly constant since 1884 despite large changes in Old Faithful's eruption intervals, suggesting that no major changes have occurred in the hydrothermal system of the Upper Geyser Basin for >120 years. Our data set provides a baseline for monitoring future changes in geyser activity that might result from varying climate, earthquakes, and changes in heat flow from the underlying magmatic system.

Components: 40,800 words, 12 figures, 4 tables.

Keywords: Yellowstone; geyser; hydrothermal; time series; tritium; water chemistry.

Index Terms: 1034 Geochemistry: Hydrothermal systems (0450, 3017, 3616, 4832, 8135, 8424); 1041 Geochemistry: Stable isotope geochemistry (0454, 4870); 1065 Geochemistry: Major and trace element geochemistry.

Received 12 August 2012; **Revised** 18 October 2012; **Accepted** 30 October 2012; **Published** 13 December 2012.

Hurwitz, S., A. G. Hunt, and W. C. Evans (2012), Temporal variations of geyser water chemistry in the Upper Geyser Basin, Yellowstone National Park, USA, *Geochem. Geophys. Geosyst.*, *13*, Q12005, doi:10.1029/2012GC004388.

1. Introduction

[2] Geysers are periodically discharging hot springs driven by steam and non-condensable gas. They are rare, with less than 1,000 worldwide, of which 200–500 occur in the geyser basins of Yellowstone National Park [*Rinehart*, 1980; *Bryan*, 1995]. Their rarity reflects the special conditions required for their formation and operation: an abundant supply of water, a large supply of heat, and a unique geometry of fractures and porous rocks [*Ingebritsen and Rojstaczer*, 1993, 1996]. In Yellowstone's geyser basins, the porous and permeable rocks consist of late quaternary kame deposits (cemented glacial till) and/or voluminous rhyolite flows covered by siliceous sinter aprons [*Muffler et al.*, 1982a, 1982b]. Because of the delicate balance between the parameters controlling their eruptions, only a few geysers display relatively constant intervals between eruptions. In Yellowstone, geyser eruption intervals (GEI) are determined using data acquired with continuously recording temperature sensors in the outflow channels of selected geysers. These data are processed, archived, and made available by the Geyser Observation Society of America (GOSA - http://www.geyserstudy.org/).

[3] Numerous studies carried out in Yellowstone's geyser basins during the past >120 years have elucidated many aspects of the dynamics of geyser eruptions [e.g., *Gooch and Whitfield*, 1888; *Jaggar*, 1898, *Allen and Day*, 1935; *Bloss and Barth*, 1949; *Marler*, 1951; *Fournier*, 1969; *Rinehart*, 1980; *Kieffer*, 1984, 1989; *Kedar et al.*, 1996, 1998; *Ingebritsen and Rojstaczer*, 1993, 1996; *Hurwitz et al.*, 2008]. Several studies have searched for correlations between external periodic forces with sub-daily cycles (barometric pressure, wind speed, and earth tides) and geyser eruption intervals [*White*, 1967; *Rinehart*, 1972; *White and Marler*, 1972; *Weir et al.*, 1992; *Rojstaczer et al.*, 2003]. The goal of this study was to search for a correlation between seasonal and decadal cycles of meteoric water recharge and GEI. We use chemical and isotopic tracers to characterize the time-dependent mixing between cold meteoric water and deep thermal water in geyser reservoirs and relate these temporal trends to eruption intervals. In particular, we test hypotheses proposed by *Hurwitz et al.* [2008] to explain seasonal GEI variations and the relation of these hypotheses to theoretical models of geyser eruptions [*White*, 1967; *Steinberg et al.*, 1981]. We search for decadal changes in the chemical composition of Old Faithful Geyser by comparing data from this study with several chemical data sets acquired since 1884. Results from this study improve the understanding of controls affecting geyser periodicity and provide constraints for physical models of geyser eruption dynamics [e.g., *Rinehart*, 1980; *Kieffer*, 1989; *Ingebritsen and Rojstaczer*, 1993; *Kedar et al.*, 1996]. The chemical data set provides a baseline for the detection of future changes in hydrothermal activity in Yellowstone's geyser basins that might result from varying climate, earthquakes, and heat flow.

[4] To achieve these goals, we sampled five geysers in the Upper Geyser Basin (Figure 1 and Table 1) up to seven times between April 2007 and September 2008 and characterized temporal variations in water major element chemistry and isotopic tracers of meteoric water recharge, $\delta^{18}O$, δD, and tritium (^3H). The five geysers studied were selected because they have relatively constant (but different) eruption intervals. The temporal eruption interval patterns of the five geysers are not in phase (Figure 2) and in some instances contrasting. For example, longer monthly average eruption intervals of Old Faithful Geyser (Figure 2c) typically coincide with shorter eruption intervals at Daisy Geyser (Figure 2d).

2. Sampling and Analytical Methods

[5] Between April 2007 and April 2008, seven water samples were collected from Aurum (ARM), Oblong (OBL), and Old Faithful Geysers (OFG) and six from Daisy (DZY) and Grand (GRN) (Figure 1), with samples obtained at intervals of approximately two months. Five additional samples from Old Faithful and Daisy Geysers and one from Aurum Geyser were collected in August and September, 2008. All samples were collected from geysers outflow channels during the main phase of the eruptions. The distances between the sample collection sites and the geyser vents differed (Table 1). Concurrent with the geyser sampling campaigns, water samples were also collected from the Firehole River near the U.S. Geological Survey gage site (http://waterdata.usgs.gov/wy/nwis/uv/?site_no=06036805&PARAmeter_cd=00065) above Upper Geyser Basin (Firehole A) and at Biscuit Basin, below the Upper Geyser Basin (Firehole B) (Figure 1).

[6] Samples for major element chemistry were collected in two clean 60 ml high-density polyethylene bottles and filtered in the field with a 0.45 μm filter. One bottle from each sample was acidified with nitric acid within 24 h for cation analysis. Raw (unfiltered) samples for $\delta^{18}O$ and δD analyses were

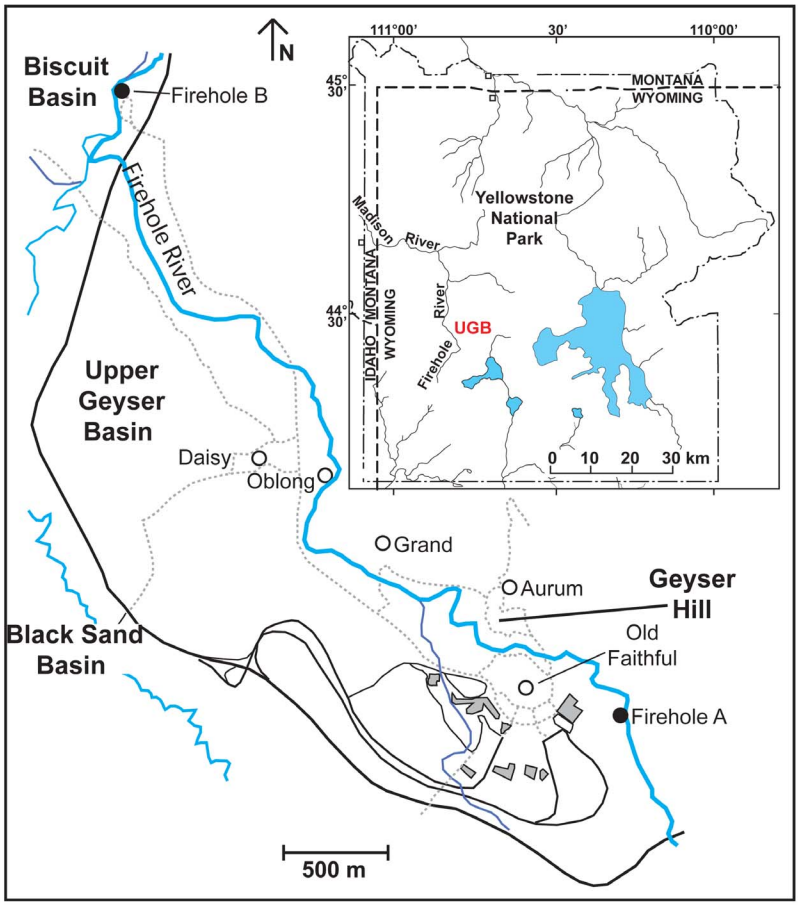

Figure 1. Map of Upper Geyser Basin (UGB) showing locations of geysers sampled in this study (open circles) and the two sampling sites on the Firehole River (filled circles). Inset: Map of Yellowstone National Park.

stored in 30 ml glass bottles, and raw samples for tritium (^3H) analysis were collected in pre-cleaned 500 ml high-density polyethylene bottles.

[7] Chemical analyses were carried out at the U.S. Geological Survey laboratories in Menlo Park, California. Concentrations of Cl^-, F^-, Br^-, and SO_4^{2-} were determined using an ion chromatograph with analytical errors of <3% for Cl^-, F^-, and SO_4^{2-} and <5% for Br^-. Total alkalinity as HCO_3^- was determined on stored samples, usually within one month after collection by titrating ten milliliters of sample with 0.05 N sulfuric acid to the bicarbonate end-point. The analytical error in the determined alkalinity concentrations is ~5%. Cation concentrations were determined using an inductively coupled plasma atomic emission spectrometer (ICP-AES). Analytical errors for Na^+, K^+, and B are typically <5%. For SiO_2 and the very low concentrations of Mg^{2+} and Ca^{2+} in the samples, the analytical errors are <10%. The charge balance RE of all samples is better than 10% (Table 2).

[8] Stable isotopes of oxygen and hydrogen were analyzed at the U.S. Geological Survey laboratories in Reston, Virginia. Oxygen isotopes were analyzed

Table 1. Geyser Type and Sampling Location

Geyser	Type	Sampling	Location	Eruption Height	Sample Collection Site
Aurum	Pool	110°49′46″	44°27′52″	~5 m	Outflow channel, <1 m from geyser
Daisy	Pool	110°50′38″	44°28′14″	~20 m	Northern outflow channel ~25 m from geyser
Grand	Fountain	110°15′14″	44°28′00″	~60 m	Outflow channel under the trail, ~35 m from geyser
Oblong	Pool	110°50′25″	44°28′09″	<5 m	4 m from trail
Old Faithful	Cone	110°49′40″	44°27′41″	30–55 m	Northern outflow channel under bridge on the trail

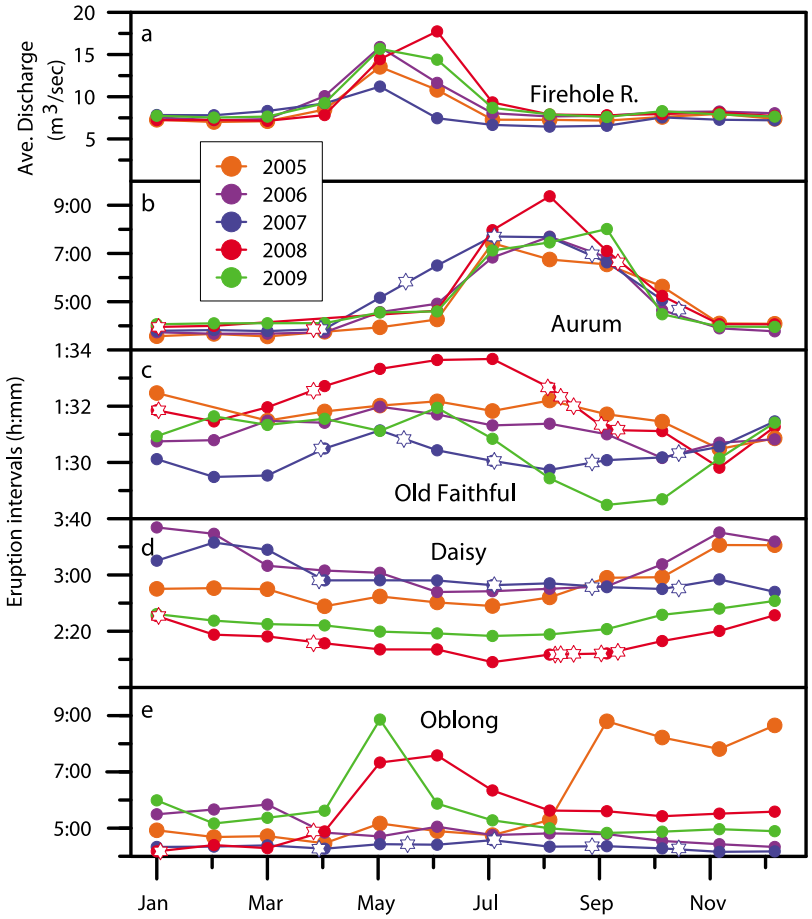

Figure 2. (a) Monthly average of Firehole River discharge at the USGS gage near Madison Junction (http://waterdata.usgs.gov/mt/nwis/uv/?site_no=06036905&PARAmeter_cd=00060,00065,00010). Monthly averages of geyser eruption intervals (filled circles and curves) between 2006 and 2009 and sampling dates in 2007 and 2008 (white stars) for (b) Aurum Geyser, (c) Old Faithful Geyser, (d) Daisy Geyser, and (e) Oblong Geyser. Data for Grand Geyser were not plotted because of the small variations.

following the methods of *Epstein and Mayeda* [1953] with a precision of ±0.1‰, and hydrogen isotopes were analyzed following the method described in *Coplen et al.* [1991] with a precision of ±1.5‰. Tritium concentrations were measured by the ^{3}He in-growth method at the U.S. Geological Survey Noble Gas Laboratory in Denver, Colorado [*Bayer et al.*, 1989]. Approximately 170 ml of unfiltered sample water was completely degassed and sealed into a vacuum flask. Tritiogenically produced ^{3}He was allowed to accumulate in the flask for approximately 100 days. The accumulated ^{3}He was extracted and measured using a magnetic sector mass spectrometer, and ^{3}H concentration was then calculated from the known decay constant of ^{3}H [*Lucas and Unterweger*, 2000] and the amount of time that the flask had been sealed. This procedure results in a lower detection limit of ~0.05 TU, where 1 tritium unit (TU) equals 1 atom of ^{3}H per 10^{18} atoms of hydrogen.

3. Chemical and Isotopic Composition

[9] Major-element concentrations, molar ratios, and δ^{18}O, δD, and tritium concentrations from the five studied geysers and from the two locations on the Firehole River are presented in Table 2 and Figures 3–8. The molar abundance of the major anions is $Cl^- > HCO_3^- > F^- > SO_4^{2-} \gg Br^-$, except for Daisy Geyser where $HCO_3^- > Cl^-$ (Figure 3a). The different HCO_3^-/Cl^- in Daisy Geyser waters as compared to Old Faithful and Aurum Geyser waters follows the distinction between Black Sand type waters (Daisy) and Geyser Hill type waters [*Fournier et al.*, 1976, 1989]. Black Sand waters have high HCO_3^- concentrations because they have undergone

Table 2. Major Element Concentrations and Isotopic Values of the Geyser Waters and Firehole River

Sample	Date	HCO_3 (mg/l)	F (mg/l)	Cl (mg/l)	SO_4 (mg/l)	Na (mg/l)	K (mg/l)	Mg (mg/l)	Ca (mg/l)	Li (mg/l)	$Si0_2$ (mg/l)	B (mg/l)	TDS (mg/l)	RE	Tritium TU	Error +/−	$\delta^{18}O$ (‰)	δD (‰)
Old Faithful Geyser																		
UGB041307-OFG	13-Apr-07	195	30	484	20	403	25	0.02	1.2	6.9	356	5.6	1529	−2%			−14.6	−132.7
UGB052807-OFG	28-May-07	197	31	484	18	389	24	<0.005	1.0	6.6	341	5.4	1498	2%			−14.3	−126.7
UGB071607-OFG	16-Jul-07	195	31	492	19	391	25	0.01	0.9	6.6	343	5.5	1511	2%			−13.4	−125.5
UGB090707-OFG	7-Sep-07	199	31	487	18	385	24	<0.005	1.0	6.5	374	5.4	1534	3%			−14.7	−132.0
UGB102407OFG	24-Oct-07	194	30	478	18	390	25	0.19	1.0	6.6	364	5.5	1514	0%	0.08	0.04	−14.7	−131.2
UGB011608-OFG	16-Jan-08	182	28	438	17	360	23	0.07	1.0	6.0	348	5.0	1409	0%			−15.6	−138.9
UGB040908-OFG	9-Apr-08	181	28	434	17	364	22	0.07	1.0	6.2	356	5.0	1416	−2%			−14.9	−128.8
UGB081408-OFG	14-Aug-08	196	35	550	23	415	26	0.01	1.1	7.1	389	5.8	1650	6%			−13.5	−129.9
UGB082108-OFG	21-Aug-08	213	34	544	21	431	27	0.01	1.0	7.4	381	6.0	1667	2%	0.21	0.10	−13.9	−129.5
UGB082808-OFG	28-Aug-08	214	33	530	20	424	27	<0.005	0.9	7.3	378	5.9	1642	2%	0.29	0.14	−13.9	−128.9
UGB091208-OFG	12-Sep-08	213	33	525	20	421	27	<0.005	0.9	7.1	347	5.9	1603	2%	0.56	0.15	−13.9	−129.1
UGB092108-OFG	21-Sep-08	194	29	454	17	372	23	<0.005	0.8	6.3	357	5.1	1459	0%			−14.3	−125.6
Daisy Geyser																		
UGB041207-DZY	12-Apr-07	684	32	332	19	508	22	<0.011	0.4	5.1	270	3.5	1877	−3%			−15.0	−134.2
UGB071607-DZY	16-Jul-07	688	33	333	18	506	22	<0.012	0.3	5.0	273	3.5	1883	−2%	0.16	0.02	−15.2	−135.1
UGB090707-DZY	7-Sep-07	719	35	357	19	541	23	<0.012	0.3	5.4	314	3.7	2020	−3%	0.21	0.07	−14.4	−131.9
UGB102407-DZY	24-Oct-07	672	32	324	17	510	22	0.18	0.4	5.1	283	3.5	1870	−6%	0.27	0.07	−15.3	−133.9
UGB011608-DZY	16-Jan-08	661	32	327	18	495	22	0.06	0.4	4.9	310	3.4	1874	−3%	0.17	0.03	−15.2	−136.3
UGB040908-DZY	9-Apr-08	691	32	326	17	510	23	0.07	0.4	5.1	295	3.5	1904	−4%	0.14	0.03	−14.9	−134.0
UGB081408-DZY	18-Aug-08	712	35	355	20	524	24	<0.012	0.2	5.2	326	3.7	2006	−1%	0.20	0.04	−13.6	−129.6
UGB082108-DZY	21-Aug-08	756	38	381	21	547	24	<0.012	0.4	5.5	315	3.8	2093	1%	0.23	0.08	−13.5	−126.7
UGB082808-DZY	28-Aug-08	697	34	342	19	520	23	<0.012	0.2	5.2	318	3.6	1961	−3%	0.09	0.09	−14.7	−134.5
UGB091208-DZY	12-Sep-08	687	33	339	19	512	22	<0.012	0.3	5.1	292	3.6	1915	−3%	0.46	0.06	−14.8	−135.4
UGB092108-DZY	21-Sep-08	648	31	320	18	478	21	<0.012	0.3	4.7	319	3.3	1845	−2%	0.21	0.03	−15.7	−138.9
Aurum Geyser																		
UGB041307-ARM	13-Apr-07	151	24	372	25	339	17	<0.012	0.8	5.6	274	4.2	1213	−8%	0.38	0.09	−15.7	−134.7
UGB052907-ARM	29-May-07	161	27	414	26	352	18	<0.012	0.8	5.8	336	4.6	1346	−2%	0.22	0.13	−15.3	−133.9
UGB071607-ARM	16-Jul-07	163	27	420	22	354	18	0.05	0.9	5.9	332	4.6	1349	−2%	0.19	0.04	−15.5	−135.5
UGB090707-ARM	7-Sep-07	164	28	441	27	364	19	<0.012	0.8	6.0	339	4.7	1395	0%	0.15	0.06	−15.2	−136.3
UGB102407-ARM	24-Oct-07	155	26	421	27	358	19	0.12	1.0	6.0	297	4.6	1316	−4%	0.32	0.05	−15.0	−135.1
UGB011608-ARM	16-Jan-08	149	24	381	25	329	19	0.05	1.0	6.3	289	4.4	1229	−5%	0.35	0.04	−15.5	−137.8
UGB040908-ARM	9-Apr-08	154	24	373	29	326	17	0.05	0.8	5.4	309	4.2	1243	−3%	0.59	0.06	−15.5	−137.2
UGB092108-ARM	21-Sep-08	153	25	408	25	343	17	<0.012	0.8	5.6	318	4.4	1302	−2%	0.27	0.06	−15.9	−139.6
Oblong Geyser																		
UGB041207-OBL	12-Apr-07	435	28	322	18	401	19	<0.012	0.4	4.7	292	3.4	1525	−3%	0.12	0.03	−16.0	−138.7
UGB053007-OBL	30-May-07	432	29	323	18	404	19	<0.012	0.4	4.7	291	3.4	1526	−4%	0.13	0.03	−16.2	−136.5
UGB071607-OBL	16-Jul-07	469	31	346	19	432	21	<0.012	0.4	5.0	303	3.7	1631	−3%	0.12	0.03	−13.9	−131.5
UGB090707-OBL	7-Sep-07	542	37	412	23	497	22	<0.012	0.5	5.9	335	4.2	1881	−1%	0.17	0.03	−13.1	−127.5
UGB102407-OBL	24-Oct-07	451	29	327	18	410	21	0.18	0.4	4.8	290	3.5	1555	−3%	0.04	0.03	−15.9	−139.0
UGB011708-OBL	17-Jan-08	450	30	334	18	414	20	0.07	0.4	4.8	303	3.5	1580	−3%	0.17	0.04	−15.8	−139.2
UGB040908-OBL	9-Apr-08	458	30	334	18	415	21	0.08	0.7	4.7	307	3.5	1593	−2%	0.29	0.08	−15.7	−137.6

Table 2. (continued)

Sample	Date	HCO_3 (mg/l)	F (mg/l)	Cl (mg/l)	SO_4 (mg/l)	Na (mg/l)	K (mg/l)	Mg (mg/l)	Ca (mg/l)	Li (mg/l)	$Si0_2$ (mg/l)	B (mg/l)	TDS (mg/l)	RE	Tritium TU	Error +/−	$\delta^{18}O$ (‰)	δD (‰)
Grand Geyser																		
UGB052907-GRN	29-May-07	382	31	392	19	419	20	<0.012	0.5	5.5	332	4.1	1608	−1%	0.06	0.07	−14.8	−133.9
UGB071611-GRN	16-Jul-07	373	31	384	17	417	19	<0.012	0.5	5.4	330	4.1	1582	−3%	0.13	0.04	−15.5	−137.9
UGB090707-GRN	7-Sep-07	372	31	388	18	423	19	<0.012	0.5	5.5	322	4.0	1584	−4%	0.01	0.04	−15.6	−137.9
UGB102407-GRN	24-Oct-07	368	30	384	17	422	19	0.22	0.6	5.4	330	4.1	1582	−5%	0.05	0.07	−15.3	−136.7
UGB011608-GRN	16-Jan-08	364	30	378	17	426	19	0.04	0.5	5.5	328	4.0	1572	−7%	0.07	0.07	−15.6	−137.4
UGB040908-GRN	9-Apr-08	371	31	386	25	415	20	0.05	0.5	5.4	326	4.0	1585	−1%			−15.4	−136.7
Firehole A																		
UGB-041207-FHA	12-Apr-07	29	3	17	4	21	4	0.46	3.96	0.10	60	0.2	144	−7%	10.11	0.21	−18.15	−134.96
UGB-052507-FHA	25-May-07	19	2	9	3	12	3	0.39	2.98	0.05	41	0.1	92	−10%	7.15	0.36	−17.77	−129.58
UGB071607-FHA	16-Jul-07	26	3	13	3	17	4	0.42	3.90	0.08	56	0.2	126	−8%			−17.94	−133.08
UGB 090707-FHA	7-Sep-07	28	3	14	3	18	4	0.42	3.98	0.08	57	0.2	131	−5%	10.16	0.34	−17.89	−131.32
UGB 102407-FHA	24-Oct-07	29	3	20	5	23	4	0.56	4.08	0.10	59	0.3	148	−9%	9.59	0.14	−17.79	−131.98
UGB 011708-FHA	17-Jan-08	31	3	20	4	24	4	0.51	4.14	0.11	63	0.3	155	−8%	9.86	0.58	−18.28	−134.67
UGB040908-FHA	9-Apr-08	31	3	22	5	26	5	0.46	4.04	0.12	64	0.3	162	−9%				
Firehole B																		
UGB-041207-FHB	12-Apr-07	85	6	46	6	62	6	0.45	4.05	0.56	87	0.6	304	−2%	9.70	0.18	−17.81	−134.60
UGB-052707-FHB	27-May-07	61	4	33	4	44	4	0.36	2.94	0.42	62	0.4	217	−1%	5.55	0.37	−17.43	−131.62
UGB071607-FHB	16-Jul-07	87	6	45	5	62	6	0.43	4.00	0.57	100	0.5	316	−1%	9.54	0.22	−17.81	−134.53
UGB 090607-FHB	6-Sep-07	82	6	42	5	57	6	0.46	4.32	0.51	87	0.5	290	−2%	10.43	0.38	−17.78	−133.22
UGB 102407 FHB	24-Oct-07	86	6	47	6	63	6	0.57	4.24	0.57	89	0.6	310	−5%	9.67	0.33	−17.64	−133.51
UGB 011808 FHB	18-Jan-08	88	6	49	6	67	7	0.48	4.43	0.61	93	0.6	323	−2%	9.24	0.44	−18.08	−136.32
UGB040908 FHB	9-Apr-08	94	7	53	6	71	7	0.51	4.20	0.64	94	0.6	338	0%	7.81	0.31	−17.89	−136.21

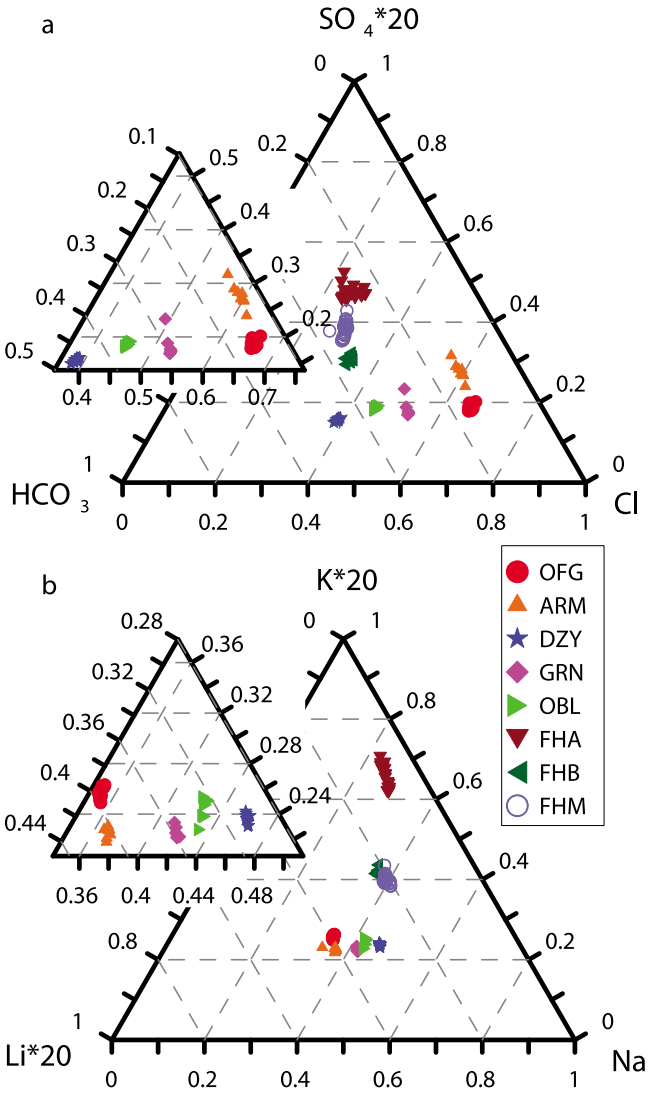

Figure 3. Ternary plots showing molar ratios of (a) anions and (b) cations of the five geysers sampled during this study and of the Firehole River above Old Faithful and at Biscuit Basin (Figure 1), and near the USGS gage near Madison Junction (http://waterdata.usgs.gov/mt/nwis/uv/?site_no=06037100&PARAmeter_cd=00060,00065,00010). The insets show the narrow range of geyser compositions.

less decompressional boiling during ascent, and thus more dissolved CO_2 remains available for conversion to HCO_3^-. The waters of Oblong and Grand Geysers have intermediate HCO_3^-/Cl^- values (Figure 3a). The waters of Aurum are slightly enriched in SO_4^{2-} as compared with the other studied geysers. The molar abundance of the major cations in all studied geysers is $Na^+ \gg Li^+ > K^+ \gg Ca^{2+} > Mg^{2+}$ and is similar to the abundance in the Firehole River which drains the geyser basins [*Hurwitz et al.*, 2010]. The concentration of Mg^{2+} in geyser waters is only several parts per billion and approaches the analytical detection limit. The concentration of Ca^{2+} in Daisy, Grand, and Oblong waters is ≤0.7 mg/l and in Aurum and Old Faithful waters Ca^{2+} concentration ranges between 0.8 mg/l and 1.2 mg/l. The cation compositions of the five geysers span a relatively narrow area on the Na^+-K^+-Li^+ ternary plot (Figure 3b). The main apparent difference is the higher Li^+/Na^+ in Old Faithful and Aurum waters (Geyser Hill type) compared with waters from Daisy (Black Sand type), Oblong, and Grand Geysers.

[10] Several chemical geothermometers are commonly used for deriving reservoir temperatures based on water-rock equilibrium [*Fournier*, 1981]. In geysers, where ascent from the reservoir is assumed to be relatively rapid, the quartz geothermometer with adiabatic cooling [*Fournier and Rowe*, 1966; *Fournier and Potter*, 1982] is probably the most

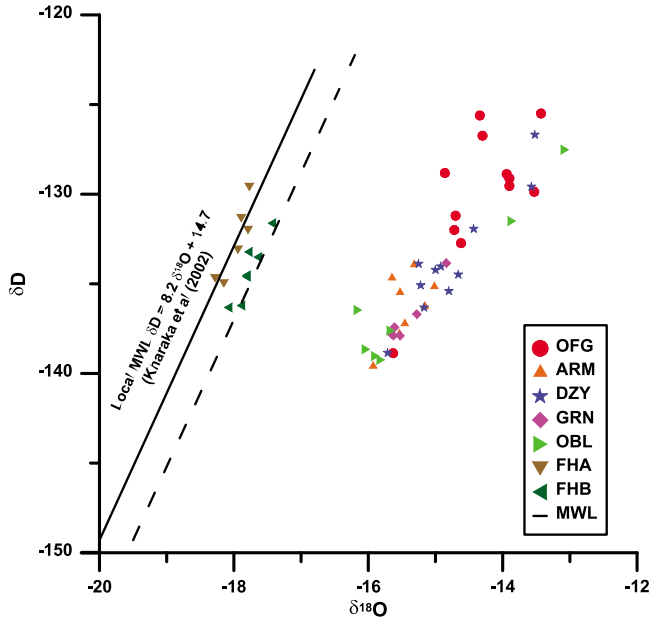

Figure 4. Water isotope compositions of the five geysers sampled during this study and of the Firehole River above Old Faithful (FHA) and Biscuit Basin (FHB). The local meteoric water line is from *Kharaka et al.* [2002]. The dashed line shows a $\delta^{18}O$ shift of 0.5‰ resulting from the influx of Upper Geyser Basin waters.

applicable, and yields temperatures ranging between 192 ± 3 for Oblong Geyser and 192 ± 4 in Daisy Geyser, to 204 ± 4 for Old Faithful Geyser. The range of temperatures derived from the quartz adiabatic geothermometer is consistent with previous estimates [*White*, 1967; *Fournier*, 1969] and with extrapolation from temperature-depth profiles in three research holes drilled in the 1960s in Black Sand and Biscuit Basins [*White et al.*, 1975].

[11] The ^{18}O values of the geyser waters are enriched by 3–5‰ compared with the local meteoric water (Figure 4). The compositions of all thermal waters in Yellowstone's geyser basins can be explained by derivation from deep thermal water of $\delta D = -148‰$ to $-150‰$ followed by boiling and steam separation upon ascent to the surface [*Truesdell et al.*, 1977]. The small variations in the δD values within each geyser, and between the geysers, likely represent varying amounts of steam separation. Waters from Old Faithful Geyser have slightly higher δD values, probably reflecting larger amounts of steam separation. The isotopic composition of waters from the Firehole River above Old Faithful (Firehole A) are similar to other meteoric water in Yellowstone [*Kharaka et al.*, 2002] and the isotopic composition of waters from the Firehole River below Old Faithful (Firehole B) are shifted from the meteoric line by ~0.5‰, reflecting mixing of meteoric water with relatively small amounts of thermal water from the Upper Geyser Basin.

[12] Tritium, which is produced in the atmosphere by cosmic ray spallation of nitrogen and decays to ^{3}He, has a half-life of 12.32 ± 0.02 years [*Lucas and Unterweger*, 2000], making it ideal for tracing modern meteoric water recharge. Modern meteoric water also contains some anthropogenic tritium introduced into the atmosphere by thermonuclear testing. A previous study found that most thermal waters in Yellowstone are mixtures of modern meteoric water and deep thermal water that contains no detectable tritium [*Pearson and Truesdell*, 1978]. Within the analytical uncertainty of our measurements, tritium concentrations in all samples from Daisy, Grand, and Old Faithful (apart from sample UGB 102407 OFG) geysers are below the analytical detection limit (0.05 TU). In contrast, all samples from Aurum and Oblong Geysers contain tritium concentrations above the detection limit (Table 2).

4. Temporal Variations

4.1. Chemical Variations Within a Single Eruption

[13] To evaluate the significance of the seasonal temporal variations we first need to assess possible chemical variations within a single eruption. Systematic studies of chemical variations within a single

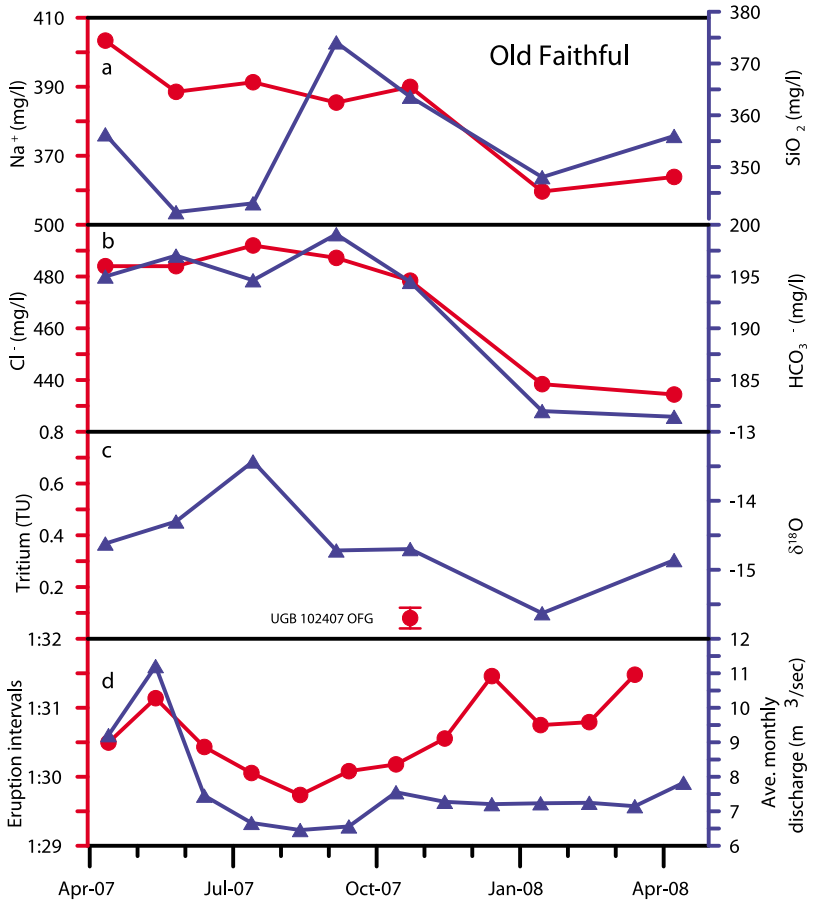

Figure 5. Temporal variation of (a) Na^+ (red symbols and curve) and SiO_2 (blue symbols and curve), (b) Cl^- (red symbols and curve) and HCO_3^- (blue symbols and curve), (c) tritium in sample UGB102407OFG (red symbol) and $\delta^{18}O$ (blue symbols and curve), and (d) average monthly eruption intervals of Old Faithful Geyser (red symbols and curve) and Firehole River discharge (blue symbols and curve).

eruption are rare. In 1962 *Noguchi and Nix* [1963] sampled an eruption of Old Faithful, but did not report the number of samples taken. They reported increasing concentrations of chlorine, alkalinity, silica and total solids from the start of the eruption to the point of highest fountaining, followed by a gradual concentration decrease as the eruption column height decreased. *Noguchi and Nix* [1963] reported a contrasting behavior for sulfate (SO_4) concentrations; these decreased after the start of the eruption and then increased as the eruption column height decreased. The overall range of reported chloride and silica concentrations varied by approximately 3%, whereas alkalinity varied by 6% and sulfate by 12%. On March 12, 1996, Steve Ingebritsen of the U.S. Geological Survey and Rick Hutchinson of the National Park Service collected water samples from two consecutive eruptions of Old Faithful Geyser; five samples were collected during the first eruption and eight samples during the second. Chloride concentrations ranged between 439.0 mg/l and 455.3 mg/l and 436.1 mg/l and 448.5 mg/l during the first and second eruptions, respectively. On the same day samples were also collected from two successive eruptions of Daisy Geyser, where chloride concentrations ranged between 316.5 mg/l and 325.7 mg/l and 320.4 mg/l and 330.3 mg/l during the first (n = 6) and second eruptions (n = 6), respectively (Steven E. Ingebritsen, U.S. Geological Survey, written communication, March 2012). The chloride concentration change between the averages of the two successive eruptions in Old Faithful or Daisy Geysers was less than 1%, which is lower than the analytical error associated with chloride concentration determinations. The variability in sulfate concentrations was significantly larger; the difference between the averages of the two eruptions is 2% and 7% in Old Faithful and Daisy Geysers, respectively. However, in general any syn-eruptive concentration variations seemed to be smaller than the analytical uncertainty.

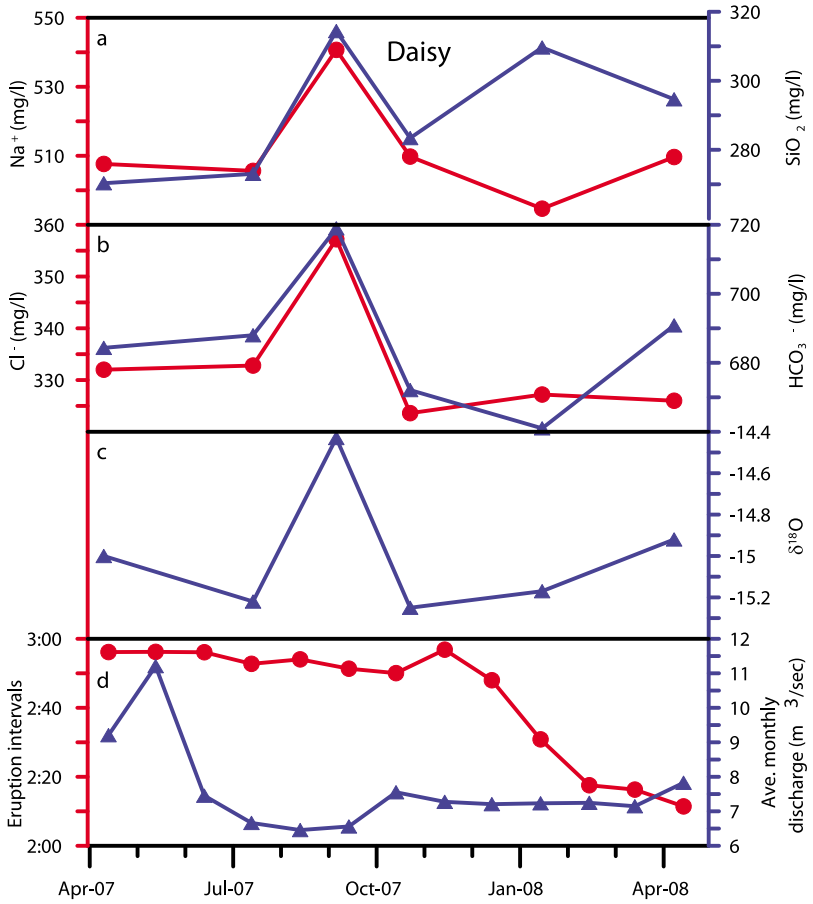

Figure 6. Temporal variation of (a) Na^+ (red symbols and curve) and SiO_2 (blue symbols and curve), (b) Cl^- (red symbols and curve) and HCO_3^- (blue symbols and curve), (c) $\delta^{18}O$ (blue symbols and curve), and (d) average monthly eruption intervals of Daisy Geyser (red symbols and curve) and Firehole River discharge (blue symbols and curve).

4.2. Seasonal Chemical and Isotopic Variations

[14] The magnitudes of the major-ion and water-isotope temporal variations in Old Faithful (Figure 5), Daisy (Figure 6), Oblong (Figure 7), and Aurum (Figure 8) geyser waters exceed the analytical errors, whereas the temporal variations in Grand Geyser waters are smaller than the analytical uncertainty. With a few exceptions, the time variation of major dissolved constituents in waters from a single geyser for the duration of our study are positively correlated (Table 3). Exceptions include SiO_2, which displays less consistent patterns; the low cross-correlation among major dissolved ions in Grand Geyser; and the negative correlation between and SO_4^{2-} and other ions in Aurum Geyser waters. Despite the significant effects of boiling and evaporation depicted in Figure 4, $\delta^{18}O$ variations are well-correlated with variations of the other major dissolved solids.

[15] To quantify the time-varying degree of mixing between thermal and dilute (meteoric) end-members [*Hurwitz et al.*, 2007, 2008], we assume that the highest concentration of each ion in all samples from a single geyser represents the concentration of the thermal end-member and we assume that the dilute end-member contains no dissolved ions. We then define the percentage by which the ion in the thermal end-member is diluted (by mass) by:

$$D = 1 - (X_i/X_{\max}) \cdot 100$$

where X_i is the concentration of the ion in the sample and X_{max} is the ion's concentration in the sample with the highest concentration (thus D = 0 in the sample with the highest concentration). The largest variations in the degree of dilution occur in Oblong Geyser (Figure 9) which is located only a few meters from the Firehole River (Figure 1). The most concentrated samples in Aurum, Daisy and Oblong geysers are from September 2007, coincident with the lowest flow rates in the Firehole River.

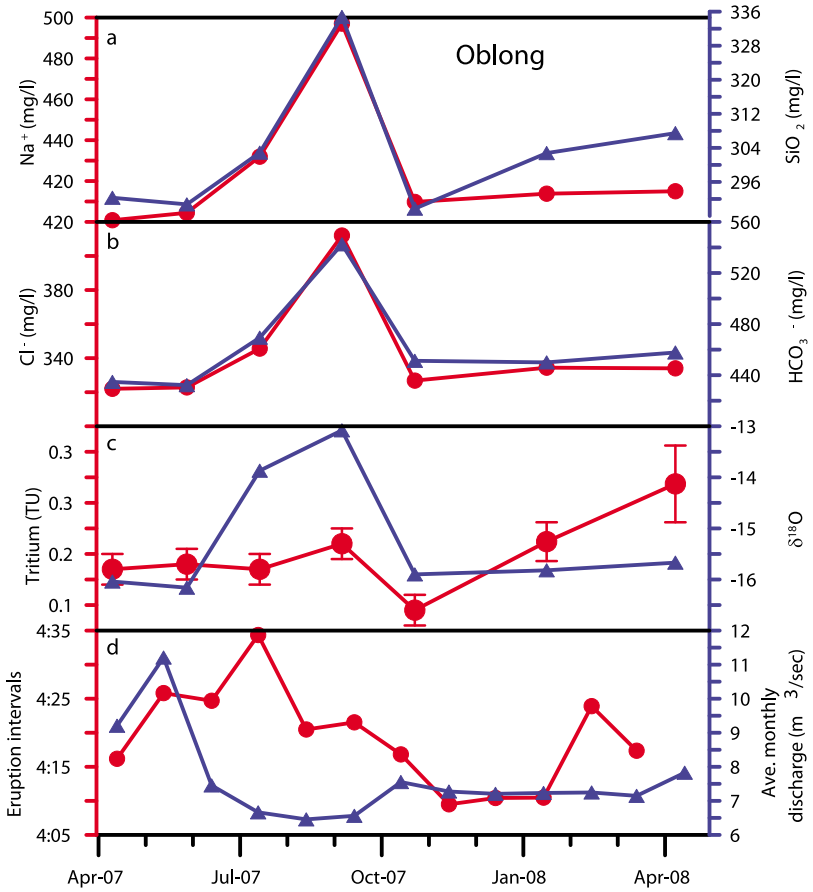

Figure 7. Temporal variation of (a) Na^+ (red symbols and curve) and SiO_2 (blue symbols and curve), (b) Cl^- (red symbols and curve) and HCO_3^- (blue symbols and curve), (c) tritium (red symbols) and $\delta^{18}O$ (blue symbols and curve), and (d) average monthly eruption intervals of Oblong Geyser (red symbols and curve) and Firehole River discharge (blue symbols and curve).

The dilution trend of Old Faithful waters differs slightly among the different major elements.

[16] The tritium content in Aurum waters (as percentage of recent tritium) was calculated assuming that the concurrent tritium concentration in the Firehole River above the Upper Geyser Basin at the Old Faithful gage (Firehole A in Figure 1) represents tritium concentrations in precipitation. In two instances no sample was available from the Old Faithful site; instead we used the concurrent tritium value from the Firehole River at Biscuit Basin (Firehole B in Figure 1). When concurrent samples from the Firehole River at Old Faithful and Biscuit Basin are available, they are consistent within 1 TU. The calculated time-varying tritium percentage is shown in Figure 9d. The thermal end-member dilution percentages calculated for the major elements in Aurum waters and those calculated separately using tritium are of the same order of magnitude, suggesting that in Aurum Geyser, seasonal variations in water chemistry are controlled by dilution with recent meteoric waters.

4.3. Decadal Chemical Variations

[17] Several studies have reported water-chemistry and eruption-interval data from Old Faithful Geyser beginning in 1884. Eruption intervals reported between 1937 and 2003 are based on visual observations from summer months by park rangers [*Stephens*, 2002]. Since 2003, year-round measurements have been made by a temperature sensor in the geyser's outflow channel (http://www.geyserstudy.org/geyser.aspx?pGeyserNo=OLDFAITHFUL). The most significant variations in Old Faithful's eruption intervals followed regional earthquakes at Hebgen Lake, Montana (1959), the Yellowstone Plateau, Wyoming (1975), and Borah Peak, Idaho (1983). Each of these earthquakes lengthened Old Faithful's intervals significantly (Figure 10a) [*Hutchinson*, 1985].

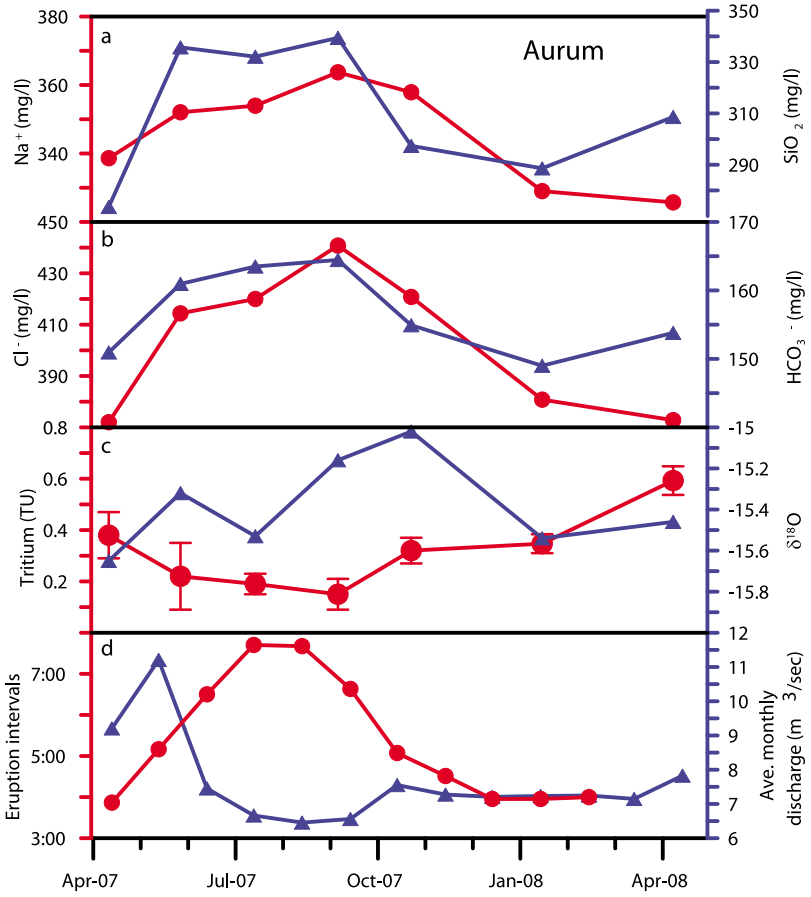

Figure 8. Temporal variation of (a) Na^+ (red symbols and curve) and SiO_2 (blue symbols and curve), (b) Cl^- (red symbols and curve) and HCO_3^- (blue symbols and curve), (c) tritium (red symbols) and $\delta^{18}O$ (blue symbols and curve), and (d) average monthly eruption intervals of Aurum Geyser (red symbols and curve) and Firehole River discharge (blue symbols and curve).

[18] Comparisons between our chemistry data and previously acquired data from Old Faithful yields information on decadal changes in hydrothermal activity and chemical changes possibly associated with the lengthening of eruption intervals. Such a comparison should be carried out with caution, because most studies have not reported the exact location of their sampling, different analytical methods were used to analyze the water and, as shown in this study, seasonal variations could be significant. Nonetheless, the concentrations of major dissolved solids (Cl^-, Na^+, and SiO_2) in the studies of *Gooch and Whitfield* [1888], *Allen and Day* [1935], *Noguchi and Nix* [1963], *Rowe et al.* [1973], *Thompson and Yadav* [1979] and the unpublished study of S. E. Ingebritsen and R. A. Hutchinson from 1996 are within range of the samples collected in 2007–2008 (Figure 10b). The Cl^- concentrations of our samples bracket all previously collected samples, whereas most previous Na^+ samples are within the lower range of our samples. Two of the samples from *Rowe et al.* [1973] have Na^+ concentrations that are slightly lower than our range. The SiO_2 concentrations in most previous samples fall within the upper range of our samples, or just above it (Figure 10b).

5. Discussion

[19] We characterized complex chemical and isotopic variations of five geysers in Yellowstone's

Table 3. Coefficient of Temporal Cross-Correlation Between Ion and Cl^-

Geyser	HCO_3^-	SO_4^{2-}	Na^+	K^+	Li^+	SiO_2
Aurum	0.85	−0.21	0.95	0.62	0.62	0.76
Daisy	0.95	0.96	0.90	0.86	0.88	0.44
Olblong	0.99	0.99	1.00	0.78	0.99	0.95
Old Faithful	0.82	0.92	0.95	0.92	0.94	0.61

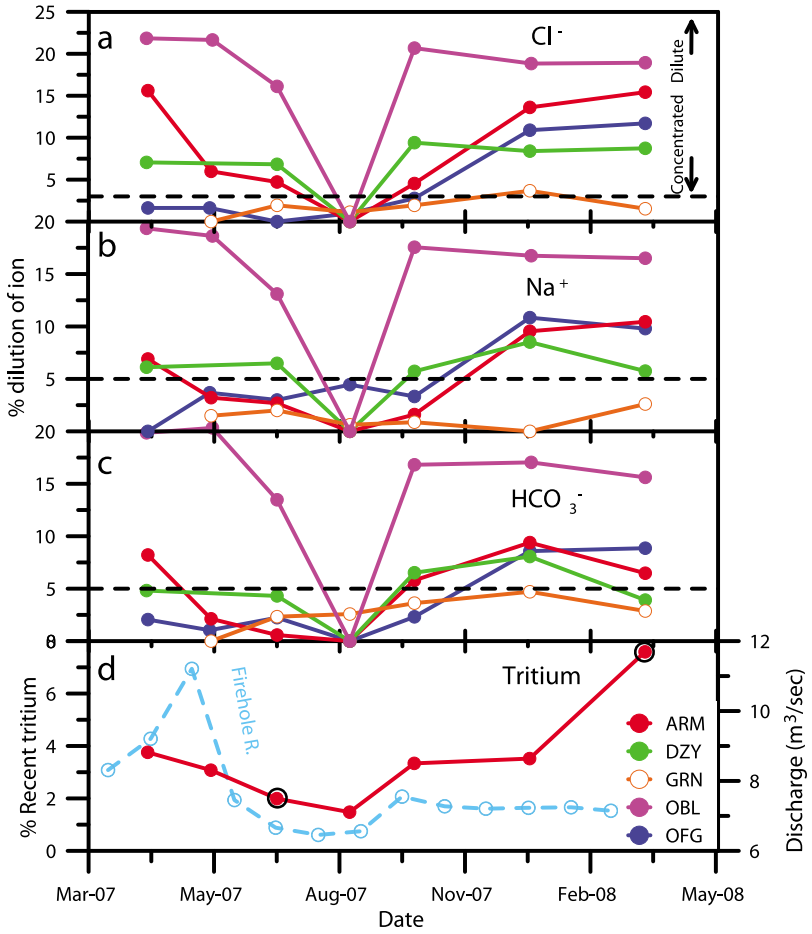

Figure 9. Percentage of dilution of the sample with the highest concentration of (a) Cl^-, (b) Na^+, (c) HCO_3^-, and (d) percentages of recent tritium in waters of Aurum Geyser (red symbols and curve) and monthly average water discharge in the Firehole River at the USGS gage near Madison Junction (light blue symbols and dashed curves).

Upper Geyser Basin. Comparison of these temporal variations with GEI variations at seasonal, inter-annual, and decadal time-scales may provide inferences on forces that control geyser eruptions. Our search for seasonal chemistry variations was motivated by the study of *Hurwitz et al.* [2008] who demonstrated that between 2003 and 2006, the eruption intervals of five geysers in Yellowstone varied in response to seasonal and inter-annual precipitation trends. In that study, it was hypothesized that variable, time-dependent mixing between deep thermal waters and shallow water recharge is the main control on seasonal and inter-annual GEI variations.

[20] Figure 2 shows that the temporal eruption interval patterns of the five studied geysers are not in phase, and in some instances contrasting, implying that each of the geysers responds differently to the parameters that control the eruption interval. This complex pattern supports the statement by *White and Marler* [1972] that "geysers are exceedingly complex hot springs, no two of which are alike." Nevertheless, the demonstrated seasonal variability in GEI and water chemistry of individual geysers implies that meteoric water recharge affects geyser eruption dynamics.

[21] To search for a possible temporal correlation between water chemistry and GEI variations, we first calculated the monthly average eruption intervals of Aurum, Daisy, Oblong and Old Faithful geysers for the period April 2007–April 2008 using data from the Geyser Observation Society of America (http://www.geyserstudy.org/) and following the averaging methods described in *Hurwitz et al.* [2008]. We then used a cubic spline function to interpolate concentrations of Cl^-, HCO_3^-, and Na^+ and the values of $\delta^{18}O$ from the 6–7 sampling campaigns to estimate monthly values. This allows the chemistry and eruption interval time series to have similar and constant temporal spacing. Due to

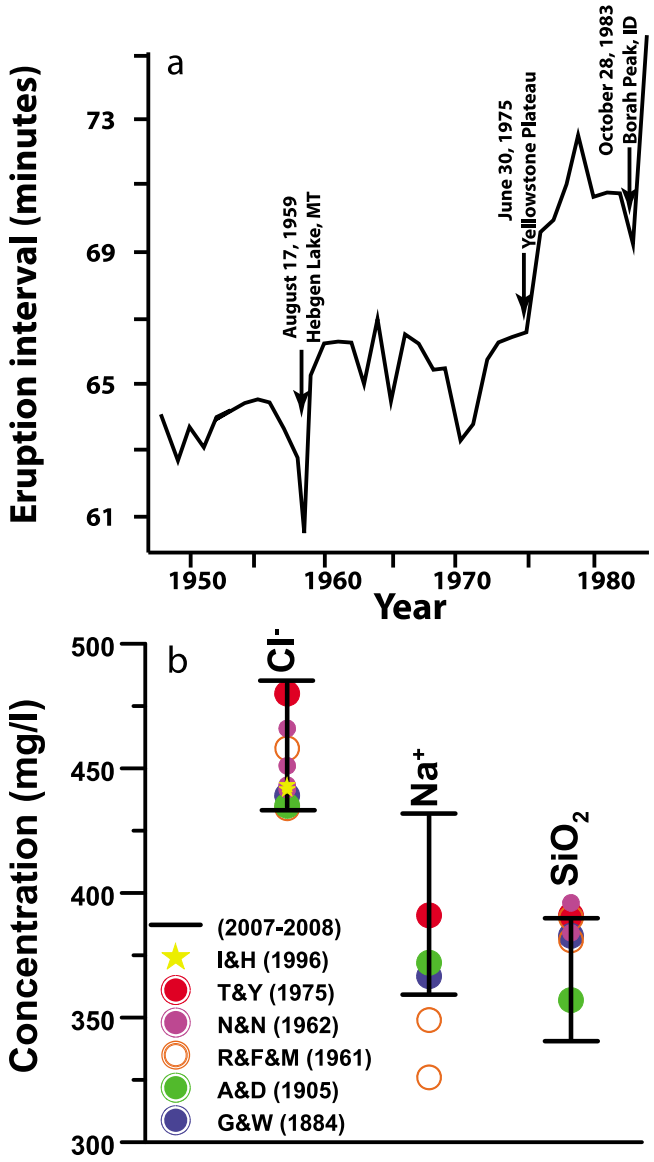

Figure 10. (a) Old Faithful Geyser average annual eruption interval between 1948 and 1984, showing the large changes following the three largest earthquakes in the Yellowstone National Park vicinity [after *Hutchinson*, 1985]. (b) Concentrations of Cl^-, Na^+, and SiO_2 in Old Faithful Geyser waters reported in the literature. G&W, *Gooch and Whitfield* [1888]; A&D, *Allen and Day* [1935]; N&N, *Noguchi and Nix* [1963]; R&F&M, *Rowe et al.* [1973]; T&Y, *Thompson and Yadav* [1979]; I&H, Ingebritsen and Hutchinson (S. E. Ingebritsen, U.S. Geological Survey, written communication, 2012). Vertical black lines bracket the range of concentrations in this study. Numbers in parentheses are the reported years of sampling.

failure of the temperature sensor at the Aurum Geyser outflow channel, no eruption interval data is available for March and April 2008. For Daisy Geyser, no sample was collected during the May 2007 campaign, so the cross correlation only covers the period between July 2007 and April 2008. The coefficients of temporal cross-correlation between the monthly averages of major constituents and the GEI are presented in Table 4.

[22] Our sampling campaign was carried out during a relatively dry year (Figure 2a and 11a) so seasonal GEI variations (with the exception of Aurum Geyser) were small compared with other years (Figure 2). The relatively dry year probably also resulted in small seasonal chemical and isotopic variations. Despite these relatively small variations, there are some consistent patterns in the cross-correlations between water chemistry and GEI (Table 4). The highest degree of cross-correlation is for Aurum

Table 4. Coefficient of Temporal Cross-Correlation Between the Variation in Ion Concentration and Oxygen Isotopes and Geyser Eruption Interval

Geyser	Cl^-	HCO_3^-	Na^+	$\delta^{18}O$
Aurum	0.79	0.95	0.70	0.10(0.47)[a]
Daisy	0.40	0.23	0.42	0.05
Oblong	0.12	0.13	0.13	0.20
Old Faithful	−0.74	−0.71	−0.58	−0.62

[a]Number in parenthesis is the calculated coefficient excluding sample UGB071607-ARM.

Geyser, which also has the largest seasonal GEI variations, and the lowest degree of cross-correlation (excluding Grand Geyser) is for Oblong Geyser which showed relatively large chemical variations but small GEI variations. The cross-correlation between GEI and $\delta^{18}O$ is low compared with the cross-correlation between GEI and Cl^-, HCO_3^-, and Na^+; this low cross-correlation may owe to variable evaporation and fractionation prior to and during the eruption. It should also be noted that one sample from Daisy Geyser (UGB090707-DZY) has a substantially higher concentration than the other five samples from Daisy (Figure 6). In addition, the GEI trend of Daisy Geyser does not display seasonality but rather a large step-like change, with more frequent eruptions beginning in December 2007. Thus, although the cross-correlation coefficients for Daisy in Table 4 are relatively high, they should be viewed with caution.

[23] The coefficients of cross-correlation are positive for Aurum, Daisy, and Oblong geysers (pool geysers – Table 1), implying that as GEIs become longer, the waters are more concentrated and the oxygen isotope values are heavier. The coefficients of cross-correlation are negative for Old Faithful (cone geyser – Table 1), implying that as GEI become longer, waters are more dilute and the oxygen isotope values are lighter. Pool geysers should perhaps be expected to be more susceptible to evaporation and input from meteoric recharge than cone geysers because they have a larger surface area in contact with the atmosphere. Nonetheless, although both Daisy and Aurum Geysers are pool geysers and display a positive cross correlation, their temporal GEI patterns are contrasting (Figures 11a and 11b), suggesting that even if evaporation and meteoric water recharge exert a strong control on GEI, the effects are complex.

[24] Geyser size (volume) also correlates with seasonal GEI and chemistry variations. Based on

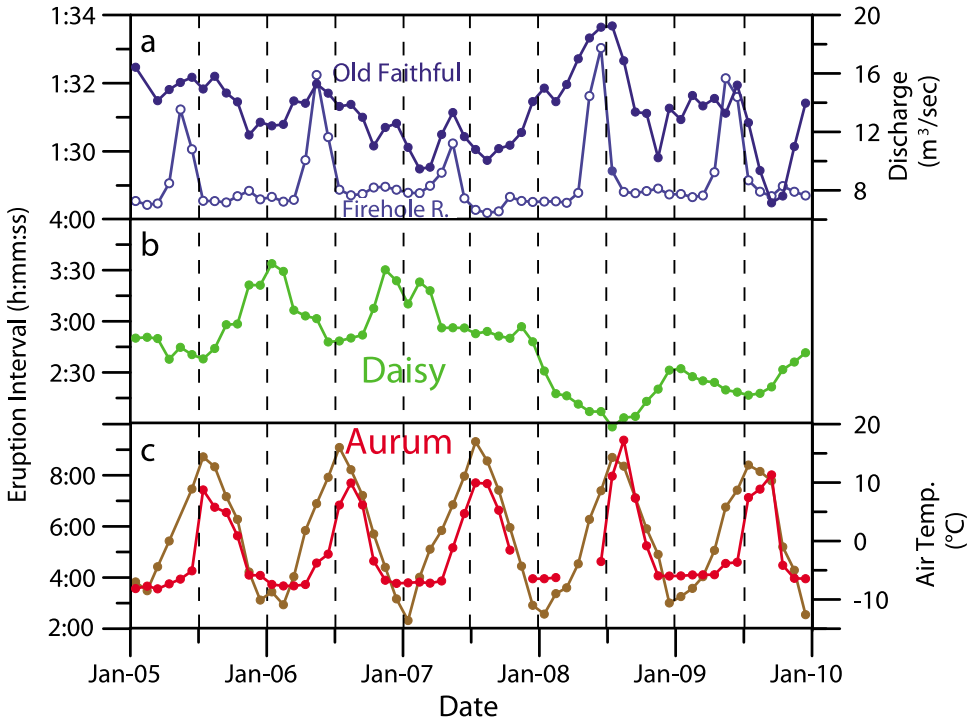

Figure 11. Monthly average values of (a) Old Faithful Geyser eruption intervals (GEI) (dark blue curves and symbols) and Firehole River discharge (light blue curves and empty symbols), (b) Daisy GEI, (c) Aurum GEI (red curve and symbols) and air temperature (brown curve and symbols) from the National Climate data Center station GHCND: USC00486845 at Old Faithful - http://www.ncdc.noaa.gov/cdo-web/customtextoptions.

visual observations, Aurum Geyser has the smallest erupted volume among the studied geysers, and has the largest temporal GEI variations (Figure 11c) and the highest tritium concentrations (Figure 7 and Table 2). Long Aurum GEIs coincide with more concentrated water, lower tritium concentrations, and higher $\delta^{18}O$ values (Figure 7). In contrast, GEI and chemistry variations in Grand Geyser (large volume) are small.

[25] Based on video observations and temperature profiles in Old Faithful Geyser, *Hutchinson et al.* [1997] proposed a hydraulic connection between the geyser and the Firehole River, ~150 m away (Figure 1). Peak annual river discharge is typically in May–June (Figure 2a) and long Old Faithful GEIs are in May–August (Figure 2c). The chemistry data presented in this study are inconsistent with an instantaneous geyser response to river levels, because high river levels coincide with more concentrated geyser waters (Figure 5). An instantaneous geyser response to high river stands is expected to result in dilute waters. In addition, no measurable tritium was detected in Old Faithful waters (except for a single exception). However, *Hutchinson et al.* [1997] suggested that "this relationship may be complex, indirect, and time dependent" and added that the groundwater level may be controlled by the Firehole River, resulting in time-dependent mixing between the cold and thermal waters. The contrasting temporal GEI pattern at Daisy Geyser, where more frequent GEIs are concurrent with high water levels in the Firehole River, suggests that in Daisy Geyser (much further from the Firehole River than Old Faithful Geyser) and possibly Oblong Geyser (near the Firehole River bank), higher water levels in the shallow subsurface shorten GEIs.

[26] To examine multiyear correlations between GEI and climate parameters (recharge, water table position, and evaporation) we plot monthly average Old Faithful (Figure 11a), Daisy (Figure 11b) and Aurum (Figure 11c) GEIs for the period 2005–2010 and compare them with monthly averages of Firehole River discharge (Figure 11a) and air temperature (Figure 11c). In 2008 when river discharge and GEI variations were largest, peak river discharge was in June–July, coincident with longest Old Faithful GEI (Figure 11a) and shortest Daisy GEI (Figure 11b). Also, in other years with smaller seasonal variations, the month with the peak river discharge roughly coincides with months of longest Old Faithful GEIs and shortest Daisy GEIs. This implies that higher recharge and water table elevation have contrasting effects on Old Faithful and Daisy GEI. Long Aurum GEIs typically in July–August are coincident with high air temperature (Figure 11c) and low river discharge (Figure 11a), suggesting strong control by evaporation and an unlikely hydraulic connection between the geyser and the river.

[27] The relatively small chemical variations in Old Faithful during the past 130 years suggest that either the subsurface reservoir is very large in comparison to the inputs (recharge) and outputs (erupted volume), or that the reservoir is small and the inputs and outputs are in a quasi-steady state. The first option is consistent with results from a tracer experiment carried out in 1963 which revealed that more than 24 consecutive eruptions were required to clear Old Faithful Geyser of introduced rhodamine dye [*Fournier*, 1969]. Reported measurements of erupted volume from Old Faithful in *Allen and Day* [1935] and *Kieffer* [1984] differ by more than an order of magnitude. Nevertheless, the second option is less likely, because annual and decadal variations in precipitation in Yellowstone National Park can be significant.

[28] In a paper titled "Is Yellowstone Losing Its Steam? Chloride Flux Out of Yellowstone National Park," *Friedman and Norton* [2007, p. 291] proposed that "The rapid decline in output of thermal-chloride flux from the Yellowstone National Park hydrothermal system documented by this study, added to the decrease in the frequency of eruptions of Old Faithful Geyser give cause for concern." This conclusion is inconsistent with the data presented in this study which suggests that no major chemistry and temperature variations have occurred in Old Faithful's reservoir since at least 1884 (Figure 10b) and that large GEI variations are mainly associated with large earthquakes (Figure 10a) which may change subsurface permeability [*Ingebritsen and Rojstaczer*, 1993, 1996].

[29] Despite the complex and contrasting temporal variations in GEI and chemistry, we propose a general model to explain the effects of meteoric water recharge on geyser periodicity that is based on the chemical and isotopic data set and the associated analysis (Figure 12). Chemical geothermometry implies that a thermal reservoir at 190–210°C which has a much larger volume than its inputs and outputs feeds all the geysers in the Upper Geyser Basin. At shallow levels, small geysers (Aurum) are more affected by meteoric water recharge and pool geysers (Aurum, Oblong, and Daisy) are more affected by evaporation. In Old Faithful and Daisy geysers shallow water table variations appear to control seasonal patterns, but in a contrasting way,

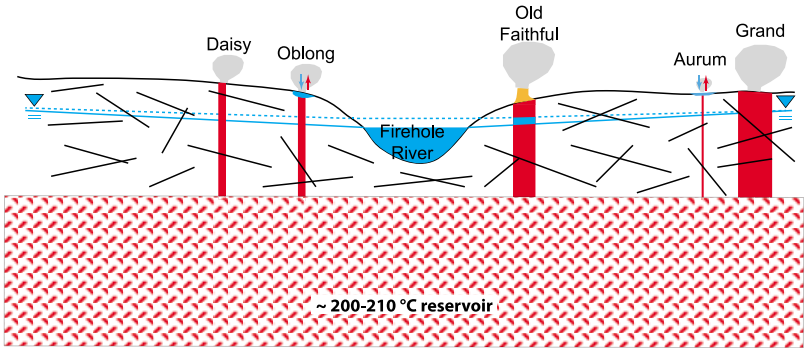

Figure 12. Schematic illustration (not to scale) showing some of the controls on geyser dynamics. A thermal reservoir at 190–210°C which has a much larger volume than its inputs and outputs feeds all of the geysers in the Upper Geyser Basin. At shallow levels, geysers are affected by meteoric water recharge and evaporation, as represented by the vertical blue and red arrows above Aurum and Oblong Geysers where these effects are most apparent. At Old Faithful and Daisy geysers, shallow water table variations appear to control seasonal patterns, though in a contrasting way. Very small variations in water chemistry in Grand Geyser suggest minor effects of meteoric water recharge, evaporation, and water table variations. The thickness of the conduit connecting the thermal reservoir to the geyser, and the size of the (gray) eruption cloud approximately represents the relative size of the geysers; Aurum is the smallest and Old Faithful and Grand are the largest.

probably resulting from a different subsurface permeability structure [*Ingebritsen and Rojstaczer*, 1993, 1996]. In Grand Geyser, very small variations in water chemistry suggest minor effects of meteoric water recharge, evaporation, and water table variations, suggesting a large subsurface reservoir.

6. Conclusions

[30] The data set presented in this study provide constraints for physical models of geyser eruption dynamics and a reference for monitoring future changes in geyser activity that might result from varying climate, earthquakes, and changes in heat flow from the underlying magmatic system. On the basis of this data set and the associated analysis we conclude the following:

[31] 1. Based on SiO_2 concentrations and geothermometry and in accord with previous studies, we conclude that geysers in Yellowstone's Upper Geyser Basin are fed by waters that ascend from a reservoir with temperatures of ~190 (Black Sand type) to 210°C (Geyser Hill type).

[32] 2. The temporal eruption interval patterns of the five studied geysers are not in phase and in some instances contrasting, implying that each of the geysers responds differently to the parameters that control the eruption interval.

[33] 3. Old Faithful, Daisy, and Oblong geysers display small seasonal chemical and isotopic variations, whereas Aurum Geyser displays the largest chemical variations of the geysers studied. Chemical variations in Grand Geyser are smaller than the analytical uncertainties.

[34] 4. Detectable tritium concentrations were measured in Oblong and Aurum Geysers, suggesting that the erupted water contains some recent meteoric water.

[35] 5. Seasonal cycles of evaporation, meteoric water recharge, shallow water table elevation, and possible hydraulic interaction with the Firehole River alter geyser eruption intervals. Eruption intervals and chemistry of geysers with smaller volume (e.g., Aurum Geyser) are more variable than those of geysers with larger volumes (e.g., Grand and Old Faithful Geysers).

[36] 6. The concentrations of major dissolved species (SiO_2, Cl^-, Na^+) in Old Faithful Geyser waters have remained nearly constant since 1884 despite large variations in the eruption intervals. This suggests that no major changes have occurred in the underlying hydrothermal system.

Acknowledgments

[37] We thank Deb Bergfeld, Laura Clor, Sean Eagan, Jake Lowenstern, Dan Mahony, and Ralph Taylor for help with sampling; Mark Huebner, Deb Bergfeld, and Haiping Qi for chemical and isotopic analysis; and Christie Hendrix, Stacey Gunther, and Hank Heasler at the Yellowstone Center for Resources in Yellowstone National Park for assistance with permitting and logistics. Steve Ingebritsen, two anonymous

reviewers, and associate editor Colin Wilson are thanked for helpful comments. This study was funded by the U.S. Geological Survey Volcano Hazards Program.

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